Removal Of Pb(II) Using Bio-Char from Microwave Pyrolysis Carbonization of Water Hyacinth

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Abstract: Water hyacinth is an invasive plant which breeds very quickly. It had led to many adverse environmental events such as river blockages and fish endangerment. This study used microwave to pyrolysis water hyacinth and activate it to produce heavy metal absorbent and improve the removal of Pb(II). Compared with conventional method, it simplify the produce process. As the dose increased to 0.25g, the absorption efficiencies of two absorbents all achieved to nearly 100%. The results indicated that the adsorption ability of WHB is close to AWHB.

1. Introduction

Biochar is a carbonaceous material that is produced under certain temperature by the carbon-rich material (cellulosic materials, wood, straw, husk, coconut shell, animal excrement). Extraordinary high specific surface area and large amount of oxygen containing functional group was achieved due to the high-temperature pyrolysis process, which contribute to the effective heavy metal absorption. In recent years, using biochar as heavy metal absorbent has attracted increasing research interest. The Ni adsorption of the lotus root derived biochar can reach 31.45mg/g within 45 minutes after phosphoric acid treatment. Alligator-made biochar showed a significant absorption ability for lead in aqueous solution and Cu(II) absorption can reach 17.71 and 21.94 mg/g respectively for raw and fermentative pig manure. Moreover, similar research have also been done to investigate biochar made from husk, pine, bagasse and sludge. To the best of our knowledge, there are few reports on heavy mental absorbent using biochar derived from aquatic plants through microwave pyrolysis technology.

Long existed the method of making biofuel through microwave production, but only in recent years has its application in biochar production been discovered. The microwave preparation power was 700-2000W, and wave-absorbent material was added to promote the pyrolysis of the biomass. Sealed quartz glass were used in the microwave reaction with a reaction time of 3-15 minutes. Thus, compared with other pyrolysis process, microwave reaction can be easily done in the reaction chamber and have characteristics like short time consuming, high efficiency, and energy-saving.

Water hyacinth (WH), also known as Eichhornia crassipes, derives from South America and is one kind of international harmful weed. The overgrowth of this weed due to the water eutrophication has brought serious problems to the ecosystem, agriculture and people’s lives. Problem emerged on how to dispose and utilize water hyacinth effectively. On the other hand, WH have a strong absorption capability for heavy metal in solutions, with a highest adsorption rate of
75.53% in 10mg/L lead solution. Problems like overgrown WH and heavy metal pollution can be solved effectively if WH can be applied in heavy metal adsorption in water purification.

2. Methods and material

2.1 Preparation of materials

The water hyacinth (WH) prepared for biochar production was collected from Banmian reservoir in Youxi county of Fujian Province. Before use, the samples were washed several times with distilled water and dried at 105°C for 24 h. The samples were then stored in the drying cabinet before utilization. The AC was bought from Xilong Chemical Industry corporation Limited (Shantou, Guangdong, China). All chemical reagent used were of analytical grade and all solution were prepared using deionized water.

2.2 Preparation of WHB

The water hyacinth was taken from the dying oven to crushed to under 2mm, and then dried at 85°C for 24h, following by transferring the water hyacinth to drying oven and cooling to room temperature. 10g WH were put from drying oven to quartz bottles, loading relative to 2% wave-absorbing materials (WHB prepared by previous time), and then were putted into micro-wave oven (Model: CM-02S, Frequency: 2.45GHz, Cemu technology company, Nanjing, China), with the quartz bottles connecting with air outlet to prevent leakage. Power and activity time were set for 1100W and 3.5min respectively. When the reaction was over and the samples cooled to room temperature, deionized water was used to wash the carbon until neutral pH. Filtration was conducted using 0.45um membrane. After drying it at 85°C for 48h, the water hyacinth biochar (WHB) was then stored in drying cabinet.

2.3 Biochar activation

Two gram WHB and 500ml 2N NaOH solution were mixed in the 500ml beaker, and then were further stired in the constant temperature magnetic stirrer with a operation temperature of 85°C for 1h. Filtration was conducted using 0.45um membrane. Deionized water was used to wash the carbon until neutral pH. After drying it at 85°C for 48h, the activated water hyacinth biochar (AWHB) was then stored in drying cabinet.

2.4 Characterization of the adsorbents

The elemental compositions of AC, WHB, AWHB were analyzed respectively using the elemental composition analyzer for WH, WHB, and AWHB. After taking materials at open crucibles and putting into muffle furnace for 6h with a set temperature of 750°C, the ash content were then calculated. The materials were investigated using Nicolet 360 FTIR spectrometer (Thermo Nicolet Corporation, US) with wavenumber ranging from 4000-400cm⁻¹ by scanning at a spectral resolution wavelength of 1 cm⁻¹.

2.5 Batch absorbent experiments

Each batch of experiments were conducted in the 100ml conical flasks under temperature of 25 ± 1 °C. The stock solution of 1000mg/L Pb(II) was prepared by dissolving Pb(NO3)2 in deionized water. Then the stock solution was further diluted to 50mg/L. And solution’s pH was adjusted by 0.1M HCl and 0.1M NaOH. After pouring 100ml of certain pH of 50mg/L Pb(II) solution into conical flask, 0.2g absorbent was added. After that, the flasks were placed on the vibration shaker for 24h with setting constant rate of 98rpm. Then the solution was filtered and analyzed it with atoms
analyzer. All experiments were controlled with the dose of absorbent and the pH of heavy metal solution. All the experiments were duplicated.

The formulation of absorbent rate of Pb(II) is:

\[ \eta = \frac{C_0 - C_1}{C_0} \]

(1)

Where \( \eta \) is absorption rate of Pb(II), \( C_0 \) is concentrations of initial heavy metal solution, \( C_1 \) is concentrations of equilibrium heavy metal solution.

3. Results and discussion

3.1 Comparison of three kinds of absorbent

The efficiency of heavy metal absorbent usually is different for kinds of absorbents. Three kinds of absorbents (commercially activated carbon (AC), WHB and AWHB) were added spontaneously to the Pb(II) solution with a initial concentration of 50 mg/L and a pH of 3 in the 100ml flasks to compare metal absorption efficiency. The Pb(II) adsorption of AC was the lowest, and Pb(II) adsorption of WHB and AWHB were 99.01% and 99.66% respectively.(Fig 1). It indicates that directly using microwave to pyrolyse WH can also obtain positive absorption capacity without conventional carbonizing method. So subsequent experiments were conducted primarily comparing WHB with AWHB.

![Figure 1. Comparison of adsorption capacity with AC, WHB and AWHB.](image)

3.2 Effect of pH for Pb(II) absorption

pH usually has a great influence for metal absorption, it directly affects the Pb(II) form in the solution. Other cationic interaction with functional groups on the materials surface, thus having an impact on the efficiency of metal absorption. To research the effect of pH on heavy metal solution, each set of Pb(II) solution pH was adjusted from 2 to 7. When pH=2, WHB absorption is a little higher than AWHB. As pH was adjusted to 3, Pb(II) absorption of WHB and AWHB had a great obvious improvement, and absorption efficiency was very close. When pH was adjusted to 4, absorption of WHB started to decline, while absorption of AWHB had a little increase. With the pH improved, the absorption of both absorbents declined smoothly (Fig 2).

![Figure 2. Effect of pH on Pb(II) absorption with WHB and AWHB.](image)
At higher pH (pH ≥ 3), Pb(Ⅱ) prone to react with hydroxide, thus producing precipitation. So it is hard to come to a direct conclusion that absorption efficiency is related to pH change by this experiment. Because this experiment can’t show that the high absorption efficiency is due to absorbent or precipitation. An experiment to research the effect of pH to Pb(Ⅱ) solution should be carried out. As pH increased from 2 to 3, the concentration of Pb(Ⅱ) nearly remained unchanged. Then as pH was improved, the concentration of Pb(Ⅱ) was declined dramatically. When pH was adjusted to 7, the concentration of Pb(Ⅱ) nearly reached 0mg/L (Fig 3). So when pH was below 3, the decrease of Pb(Ⅱ) concentration was primarily due to absorbents. Therefore all following experiments were not conducted beyond the pH 3.

3.3 The effect of absorbent dose on Pb(Ⅱ) absorption

To research the relation between the absorbents dose and Pb(Ⅱ) absorption efficiency, the experiment dose were designed ranging from 0.05g to 0.25g, and other conditions remained unchanged (initial concentration: 50mg/L, pH=3, reaction time: 3min environment temperature: 25±1℃).

With increasing amount of absorbents, absorption efficiency of Pb(Ⅱ) was increasing (Fig 4). With a dose of 0.05g, two absorbent efficiencies were very similar. As the adsorbent dosage increased to 0.1g, the efficiency and growth rate of WHB were a little higher than AWHB. As the amount of dose increased to 0.15g, the absorption rate of AWHB increased dramatically, and absorption efficiency reached to 82.37%. While the absorption rate of WHB increased slower relatively to 62.21%. As two absorbents dose was increased to 0.2g, the absorption efficiencies of two absorbents all achieved above 99%. And the absorption rate of AWHB became slower than before, while the WHB had not changed. As the dose increased to 0.25g, the absorption efficiencies of two absorbents all achieved to nearly 100%.

Combined with Fig 2, despite some certain situation that 0.05g and 0.20g of two absorbents could result in similar results, the process of absorption from 0.05g to 0.20g was very different. It may be due to two absorbents had different function groups on its surface, or it had very different
structures of surface or size of holes. In Fig 2, at pH 2 the concentration of \(\text{H}^+\) was higher, the absorption of AWHB was inhibited. The phenomenon also occurred as dose increased from 0.05g to 0.10g, the absorption efficiency of AWHB was lower than WHB. When \(\text{H}^+\) decreased or the dose of AWHB increased, the inhibited effect of \(\text{H}^+\) decreased dramatically, and the absorption efficiency of AWHB enhanced dramatically. While for the absorption rate of WHB that the process of absorption from 0.05g to 0.20g was nearly unchanged. So it may show that at pH 3 reaction had reached a balance between concentration of \(\text{H}^+\) and the function groups on its surface, or the function groups of WHB was not affected by \(\text{H}^+\). It can be seen that when the concentration of \(\text{H}^+\) was high, using WHB can have a better absorption. While the concentration of \(\text{H}^+\) decreased (pH≥3), using AWHB is a smart choice to obtain a better absorption.

3.5 Function groups analysis

Fig 5 is the wavelength of the infrared spectra of 4000-400cm\(^{-1}\) for WHB and AWHB. The infrared spectra indicated that two absorbents had some similar function groups and some different function groups. The first peak for WHB and AWHB at 3430cm\(^{-1}\) and 3440cm\(^{-1}\) respectively, it indicated the existence of O-H stretching of the two adsorbents (intermolecular hydrogen bonded)\(^{16}\). WHB’s peak at 1610cm\(^{-1}\) indicated that it had C=C aromatic stretching, and peak at 1421cm\(^{-1}\) indicated that there is C-C asymmetric bending. The AWHB’s peak at 1560cm\(^{-1}\) showed the existence of C=O stretching corresponding to lactone and carbonyl. The peak at 1200-1000cm\(^{-1}\) for WHB and AWHB indicates the existence of C-O bond in carboxyl, the alcohols, the phenols, the esters, or P=O bond in phosphate esters. These surface features were analogous to the one derived from treatment of carbonization following micro-wave processing. This similarity may be attributed to the fact that lignocellulose can hardly absorb micro-wave energy while carbide possess a high capability for micro-wave energy absorption. Thus, lignocellulose can’t be obtained directly under microwave processing as carbide do and a treatment.

![FTIR absorption spectra](image)

Figure 5. FTIR absorption spectra, a) WHB b) AWHB.
is requested beforehand. For direct micro-wave processing, micro-wave absorbent, which served as a heat source, can absorb heat rapidly, causing lignocellulose carbonization through heat conduction. Carbonized lignocellulose also can absorb the microwave instantly and conduct the heat to the peripheral lignocelluloses. Ultimately all stock are carbonized with effective energy absorption. So two method can obtain similar form of function groups.

Two absorbents all had hydroxyl stretching, and potassium hydroxide doesn’t have a great influence on it. While peak at 1610-1421cm⁻¹, the function groups for two absorbents had a dramatically difference. It showed that potassium hydroxide can react with function groups on WHB surface, and change chemical structure of function groups. The peak change between 1200-1000 cm⁻¹ for two absorbents indicates that potassium hydroxide not only can change chemical structure of function groups but also remove the organic residual which can not be removed at previous time. After treated with potassium hydroxide, the AWHB had more simple function groups form, and improved the ability to combine with the Pb (Ⅱ).

4. Conclusion

Through series of experiments pH of Pb(Ⅱ) solution, dose of absorbents and comparisons with AC, WHB and AWHB, results indicates that WHB and AWHB have better absorption ability than AC, so compared with conventional method, directly using micro-wave method can obtain better capacity for absorbing Pb(Ⅱ). At pH 3, the absorption efficiency can achieve 99% with 0.2g absorbents in 50mg/L Pb(Ⅱ) solution.

Compared with conventional method, microwave pyrolysis simplify the produce process. As the dose increased to 0.25g, the absorption efficiencies of two absorbents all achieved to nearly 100%.

The infrared spectra peak vibration detected by FTIR spectrometer indicated that function groups of WHB and AWHB existed in slightly different manner but they were all similar with the function groups of pyrolysis and micro-wave assisted carbonization. The results indicated that the adsorption ability of WHB is close to AWHB

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References


